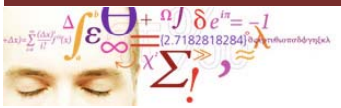
Glycoproteins at the rubbing interfaces of biosystems

Lee, Seunghwan

Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record



Glycoproteins at the Rubbing Interfaces of Biosystems

4th Workshop in Proteins.DTU
November 12, 2010, DTU

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Department of Mechanical Engineering

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Water as a lubricant

Oil

Men's primary choice of lubricant

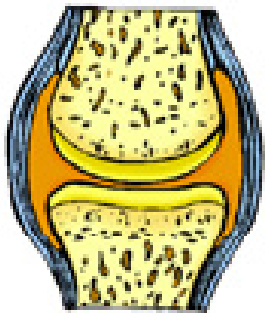
Challenges in oil-based lubrication:

limited resources

environmental issue (especially additives)

Water

Nature's primary choice of lubricant



Synovial Joint

μ for human cartilage: as low as 0.001!

Water as a lubricant in engineering point of view

- non-toxic
- environmentally-friendly
- readily available and cost effective
- non-flammable
- high thermal capacity
- biocompatible

- poor pressure response

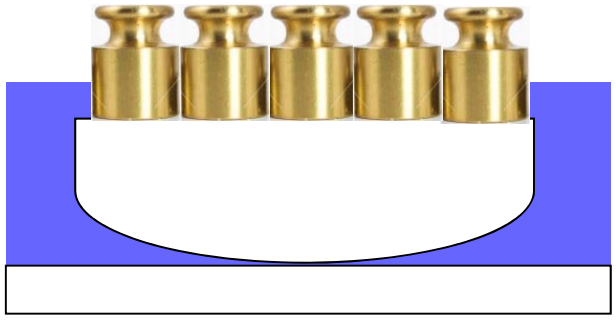
low pressure-coefficient of viscosity

water: α = 0.36 GPa^{-1}

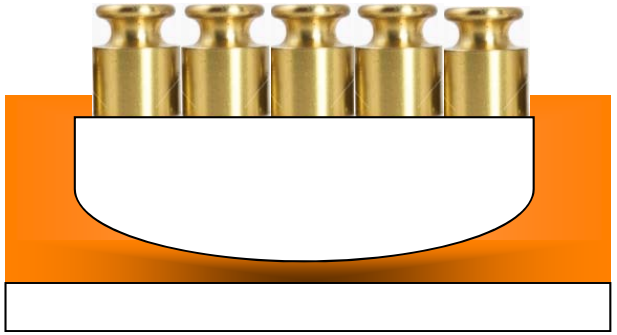
oil: α = 10-20 GPa^{-1}

- limited application temperature
- corrosion for ferrous materials

water

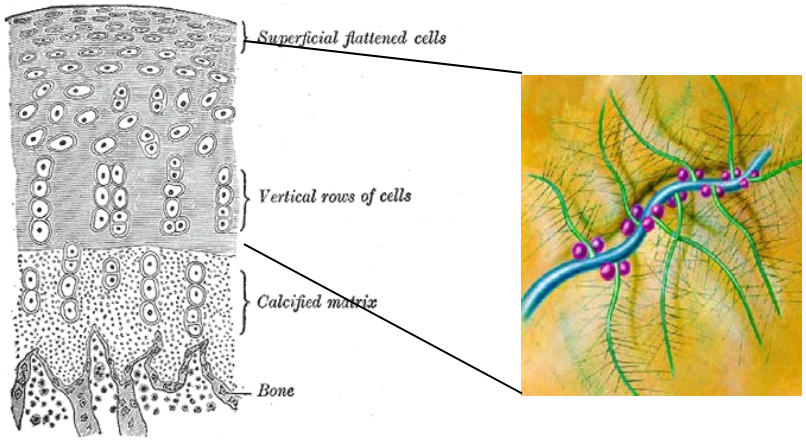


oil



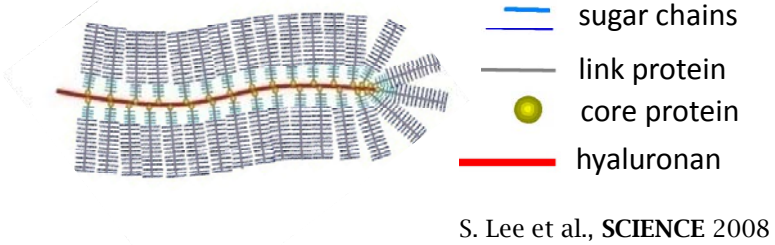
Nature's approach to use water as lubricant

brush-like*, *sugar-based
macromolecules



Proteoglycan aggregate

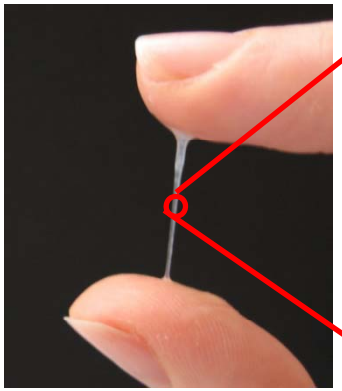
- plays a key *structural role* in cartilage



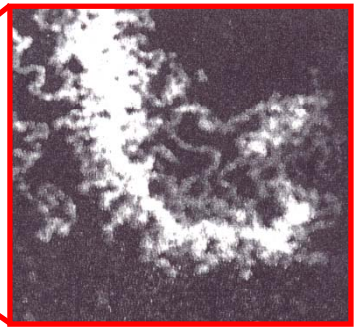
S. Lee et al., **SCIENCE** 2008

Mucins

Mucus (gel)



Mucin (polymer)

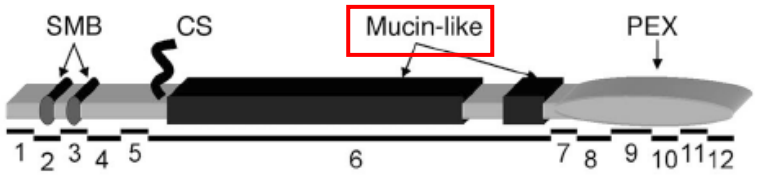


PGM
(STM, 360 nm × 360 nm)

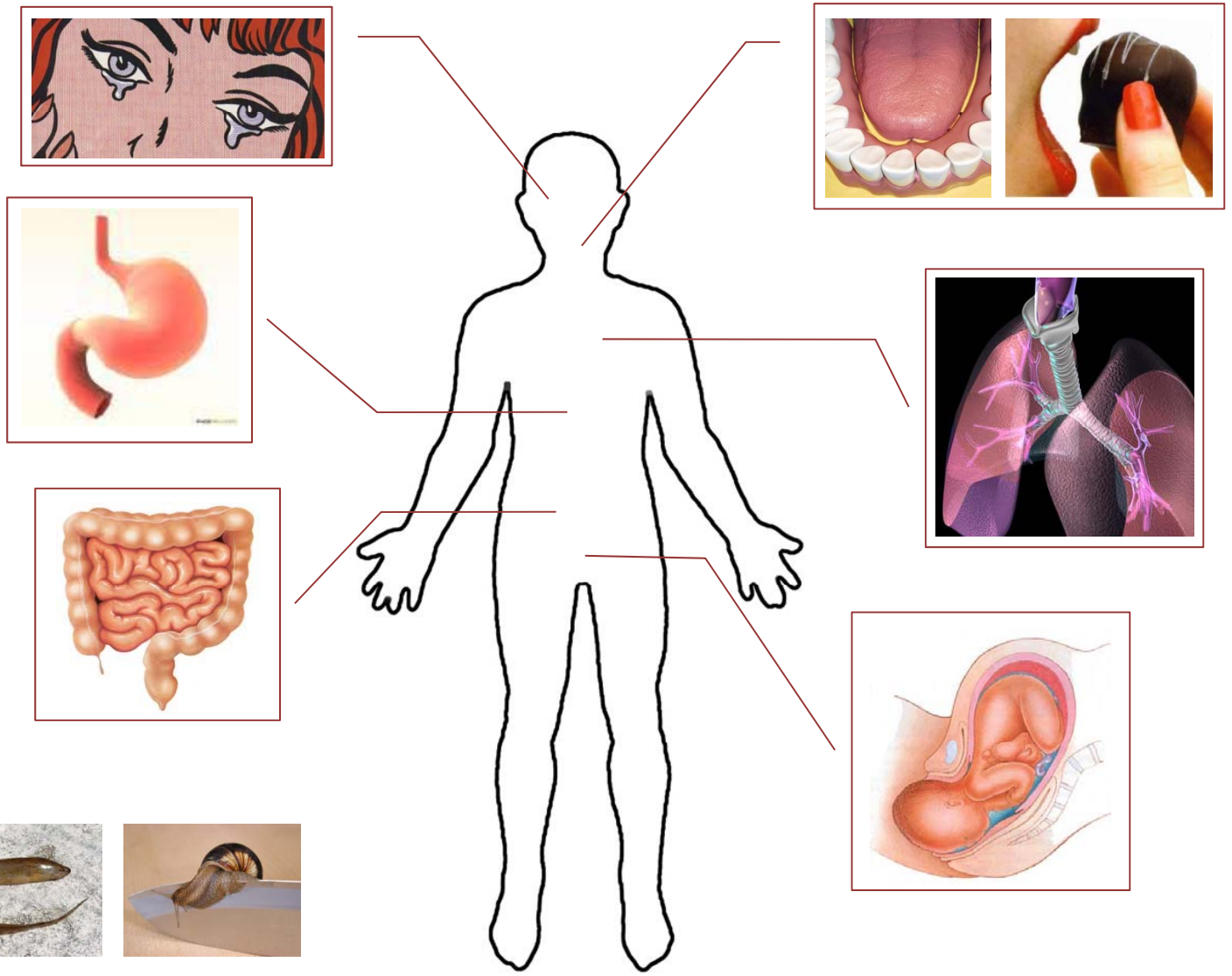
Roberts, CJ et al Proteins and Peptide Letters 1995 2, 409

Lubricin

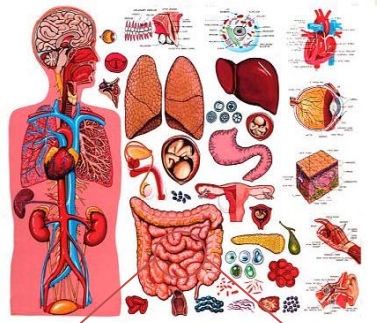
- mucinous glycoprotein of the synovial fluid (250 µg/ml, MW = 2.3 × 10^5 g/mol)



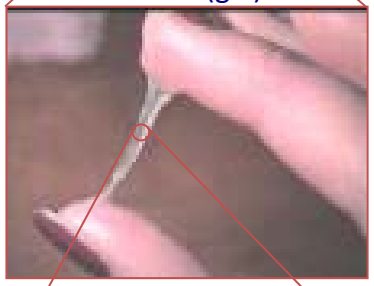
Lubricity of mucins/mucus gels



Mucus, Mucin, and Mucin Domains



mucus (gel)



Water

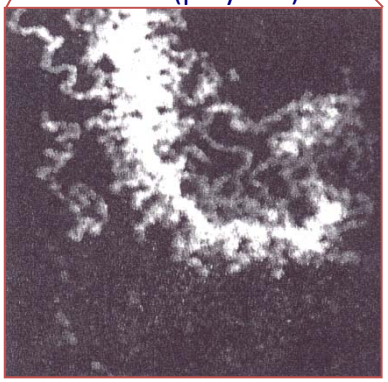
Salts

IgG

Proteins

mucins

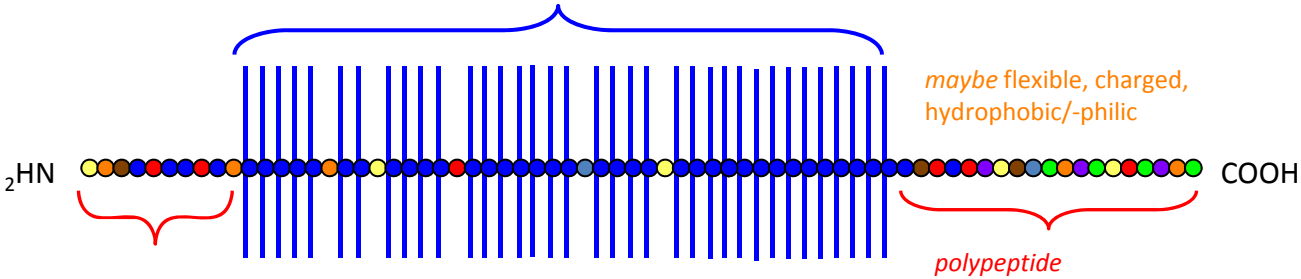
mucin (polymer)



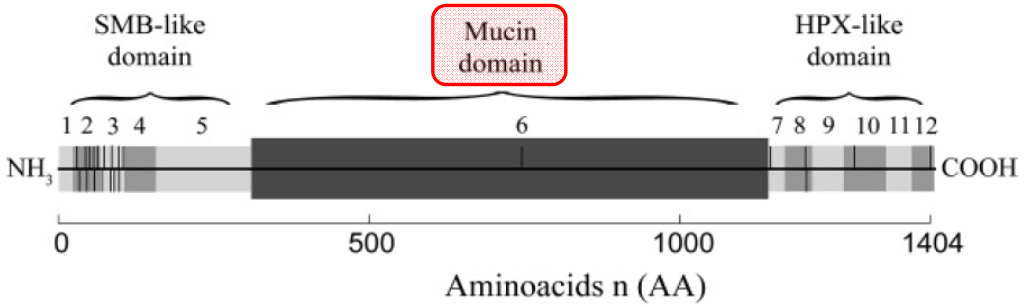
PGM, STM (360 nm ⍰ 360 nm)

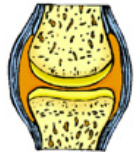
Roberts, CJ et al, **Proteins and Peptide Letters** 1995, 2, 409

Schematic representation of the mucin



Schematic representation of the Lubricin (PRG 4)

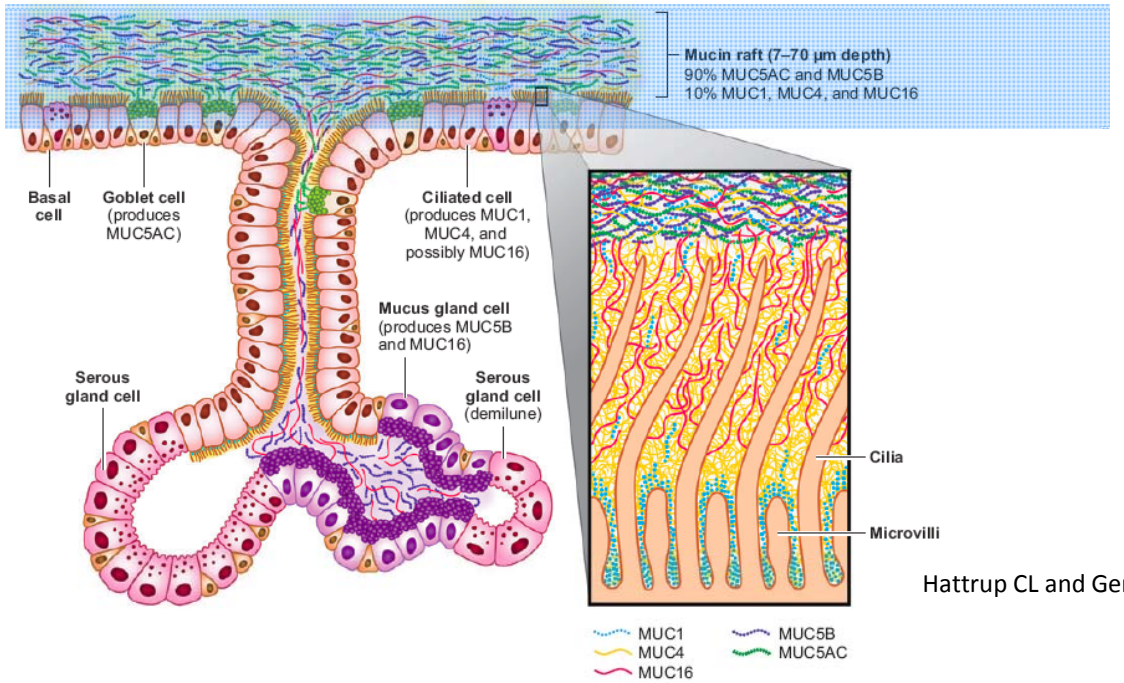




Synovial Joint

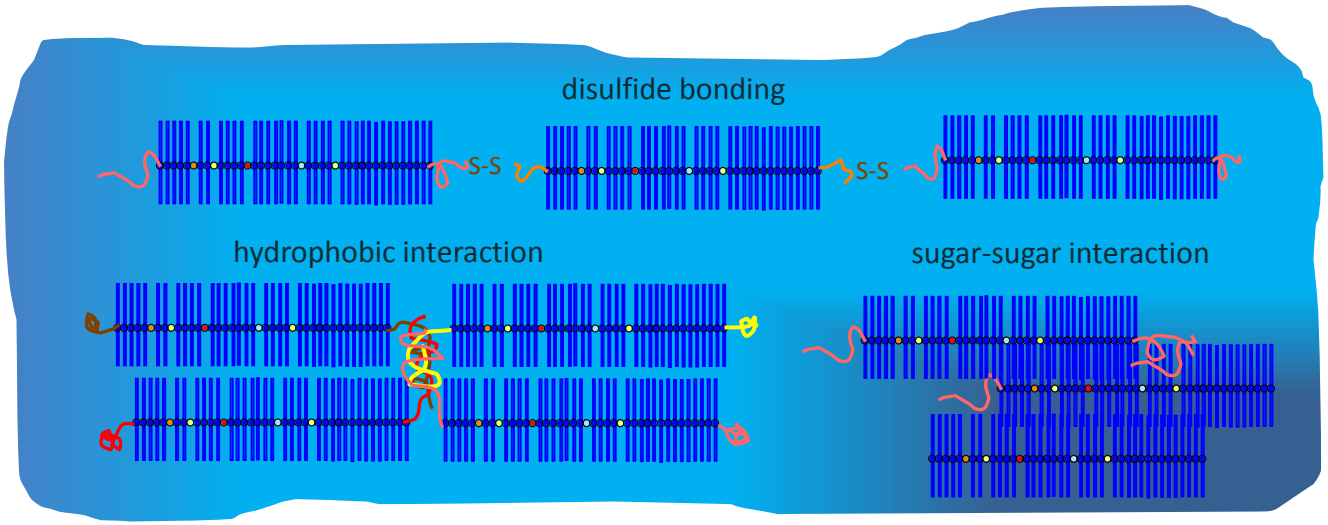
Zappone B et al, Langmuir **2008**, 24, 1495.

Mucus gels



Hattrup CL and Gendler SJ, *Ann. Rev. Physol*. **2008**, 70, 431

Gel-formation (in vivo)



Monolayer of mucins at water/solid interface

- Hydrophilicity

  L. Shi and K.D. Caldwell, *J. Colloid & Interf. Sci. (2000)* 224, 372-381

- Suppression of proteins and bacteria adsorption

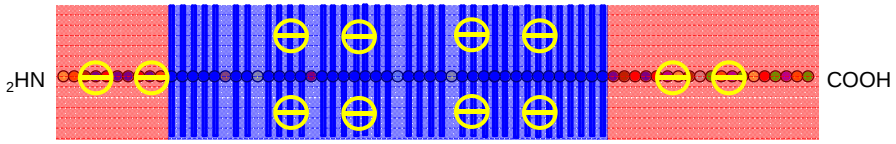
  L. Shi, R. Ardehali, P. Valint, & K.D. Caldwell, *Biotech. Letters (2001)* 23, 437-441

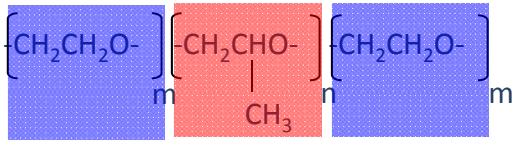
- Lubrication

  I.C.H. Berg, L. Lindh & T. Arnebrant, *Biofouling (2004)* 20, 65-70

  S. Lee, M. Müller, K. Rezwan, N.D. Spencer, *Langmuir (2005)* 21, 8344-8353

Mucins as a amphiphilic copolymer





Model surface and pin-on-disk tribometry

Elastomer as model surface of biological tissues: mimic mechanical properties

Poly(dimethylsiloxane) (PDMS)

Young´s modulus

ca. 2 MPa

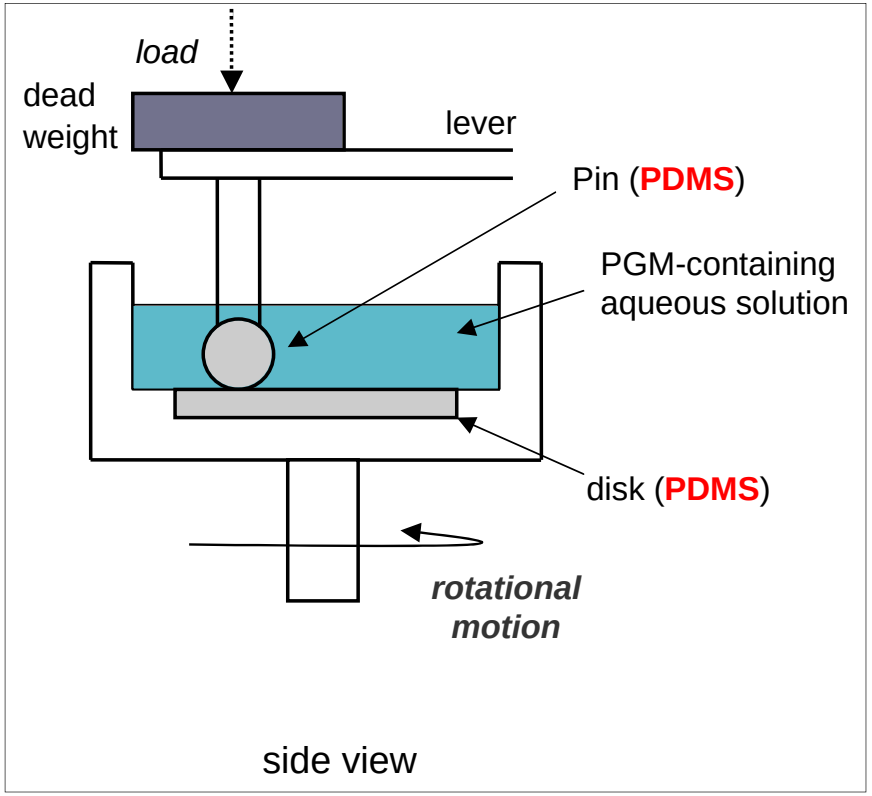
Poission ratio

0.5

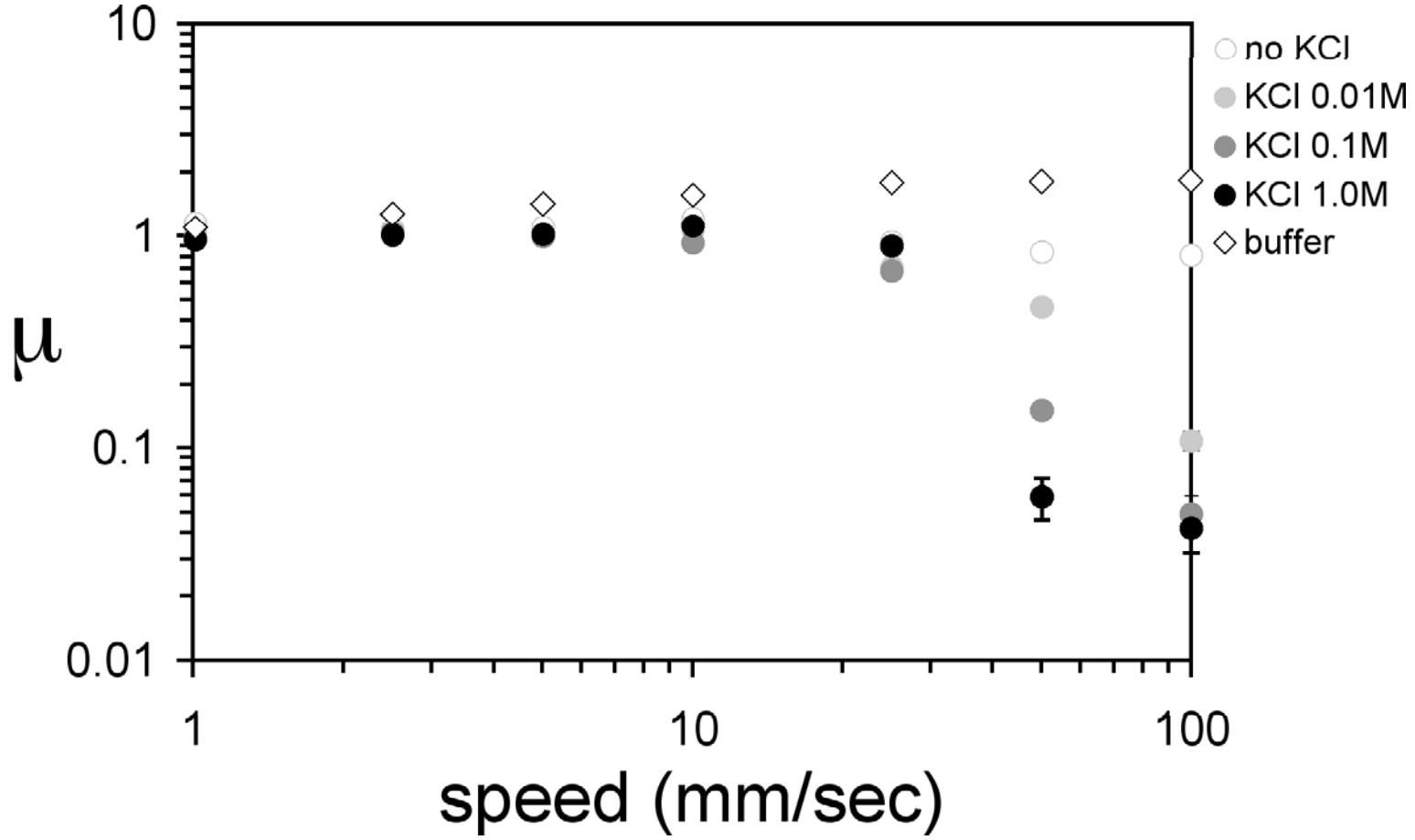
Load = 1 N

P ~ 0.5 MPa

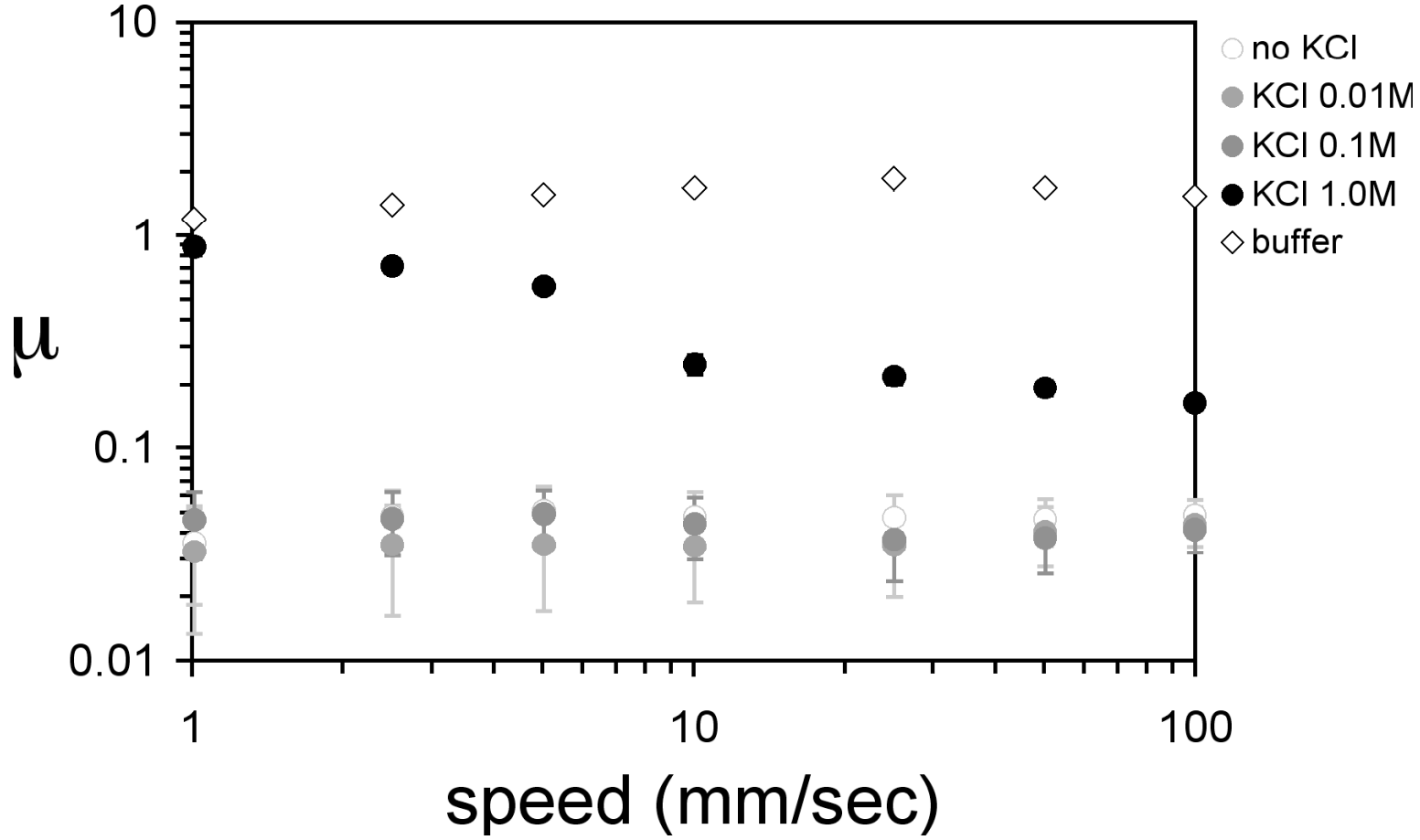
pin-on-disk tribometer



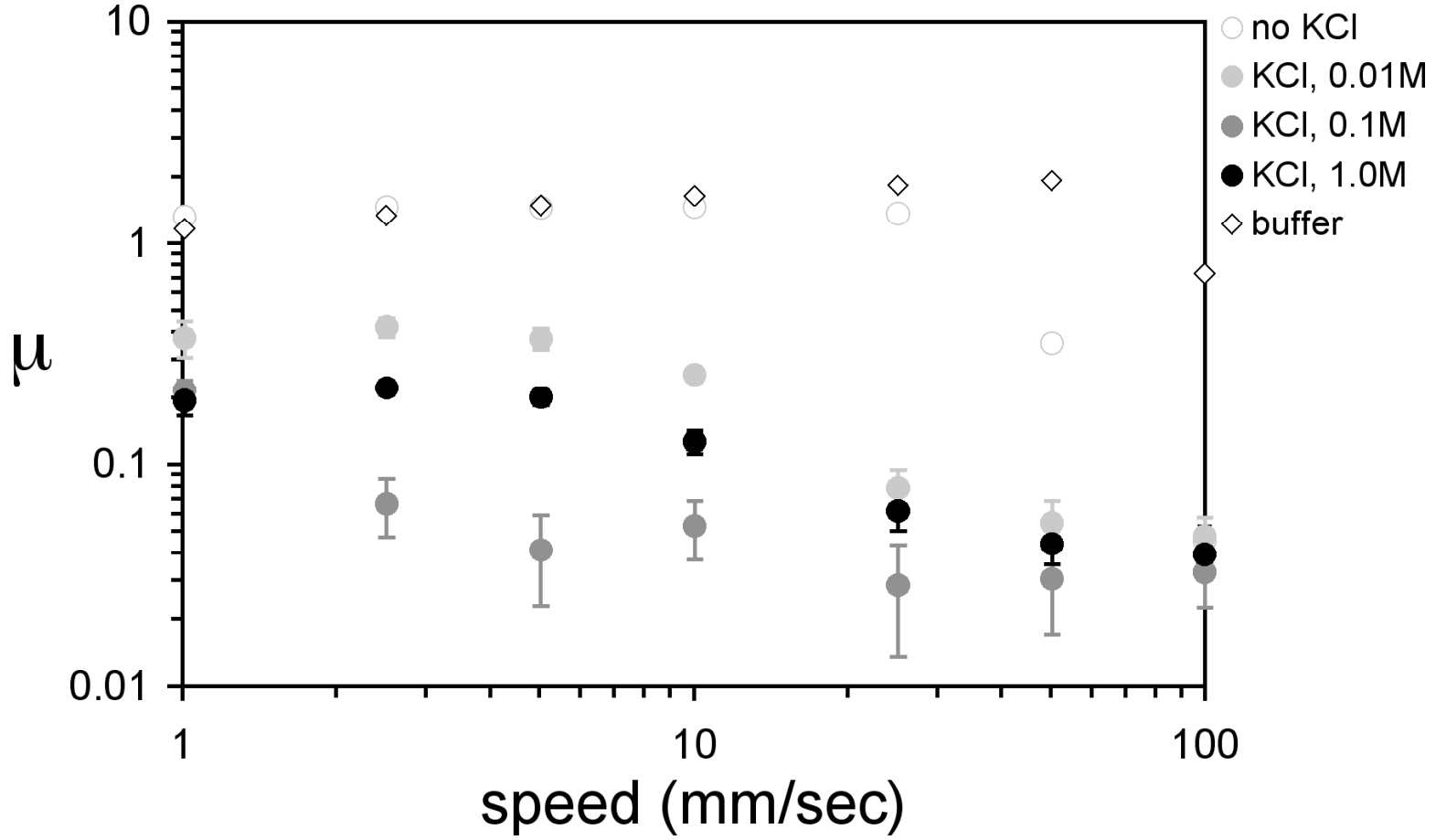
Lubrication properties of PGM solution: pH 7



Lubrication properties of PGM solution: pH 2



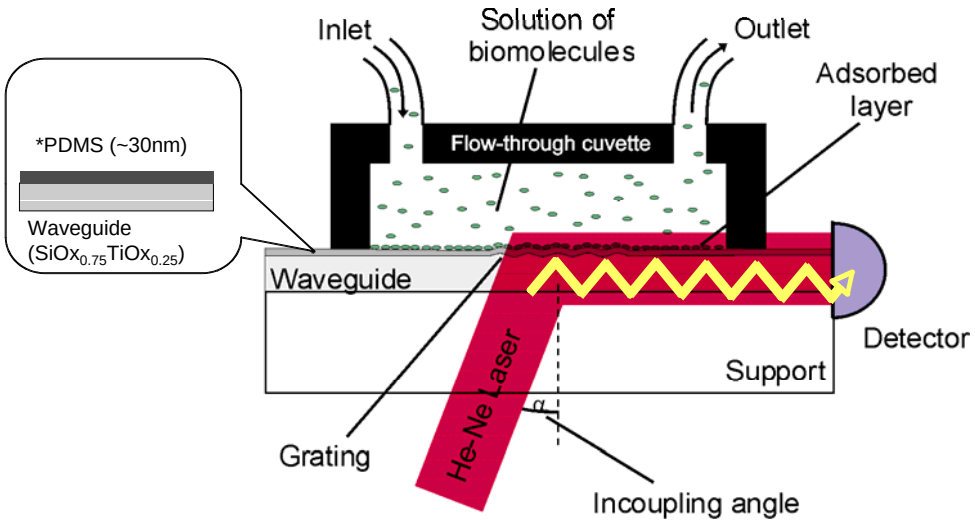
Lubrication properties of PGM solution: pH 12

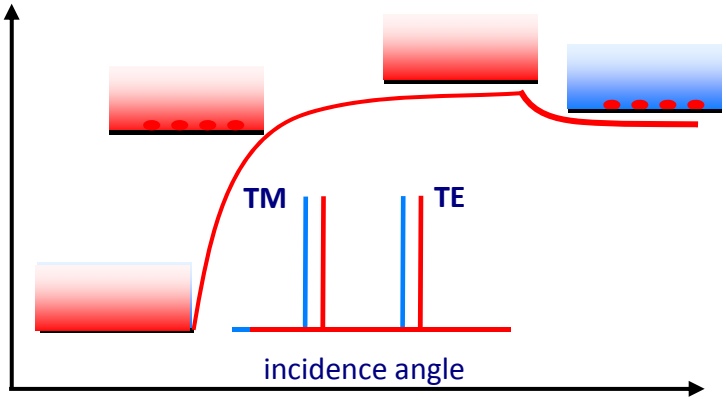


Surface adsorption properties: OWLS

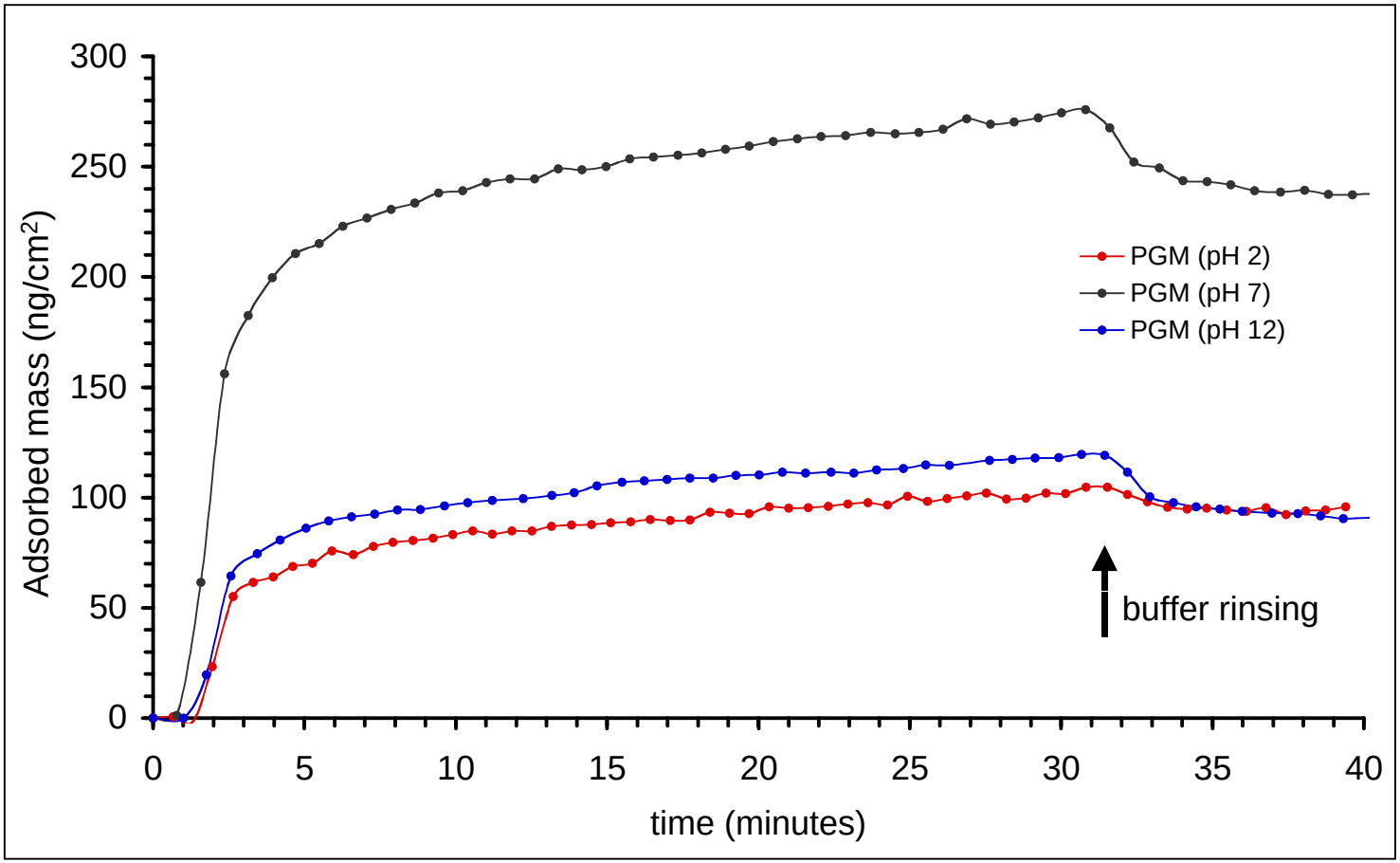
*O*ptical *W*aveguide *L*ightmode *S*pectroscopy (*OWLS*)

Adsorption of mucins onto PDMS surface





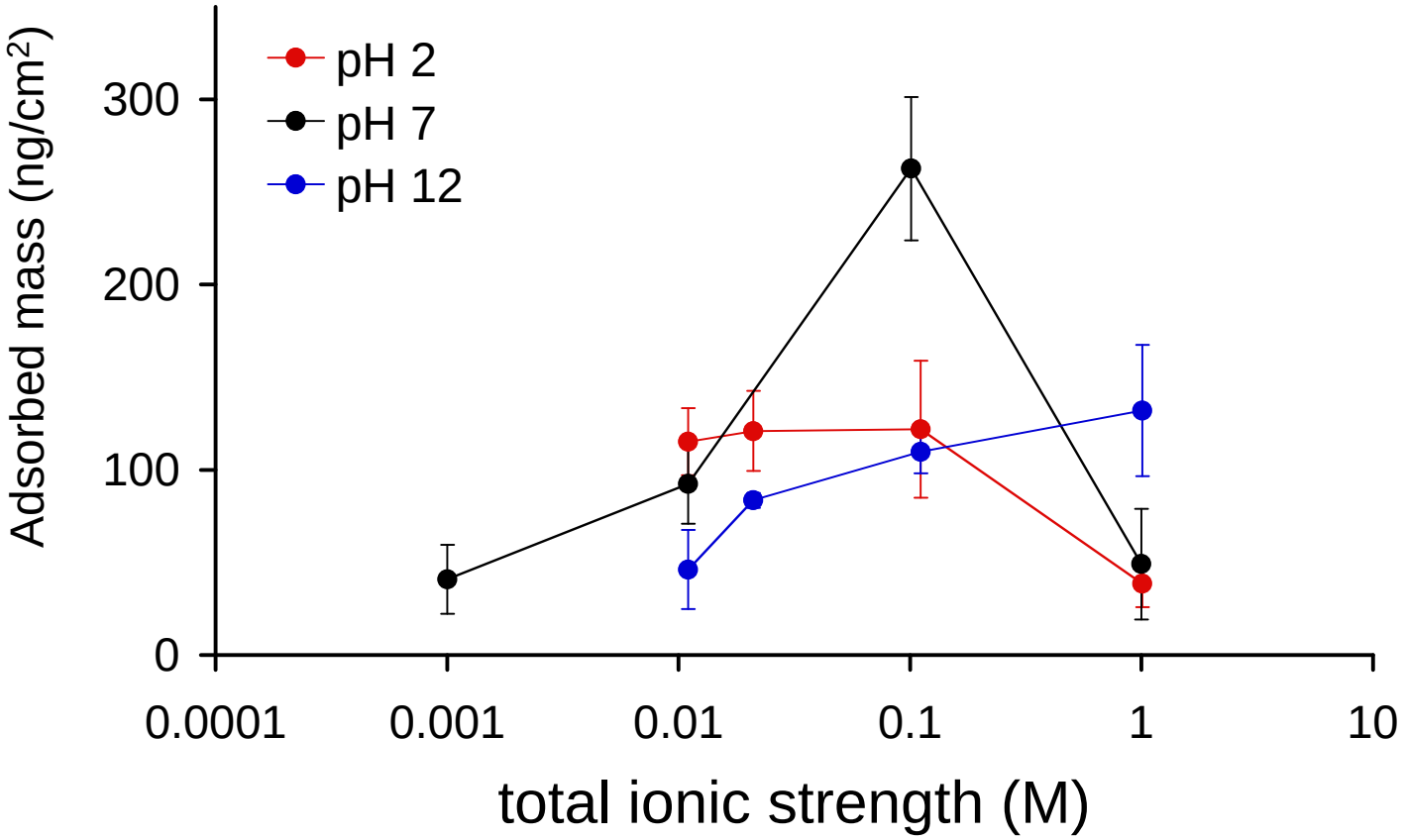
Surface adsorption properties: OWLS



PGM, 1mg/ml buffer: 1mM KH_2PO_4, KCl 0.1M

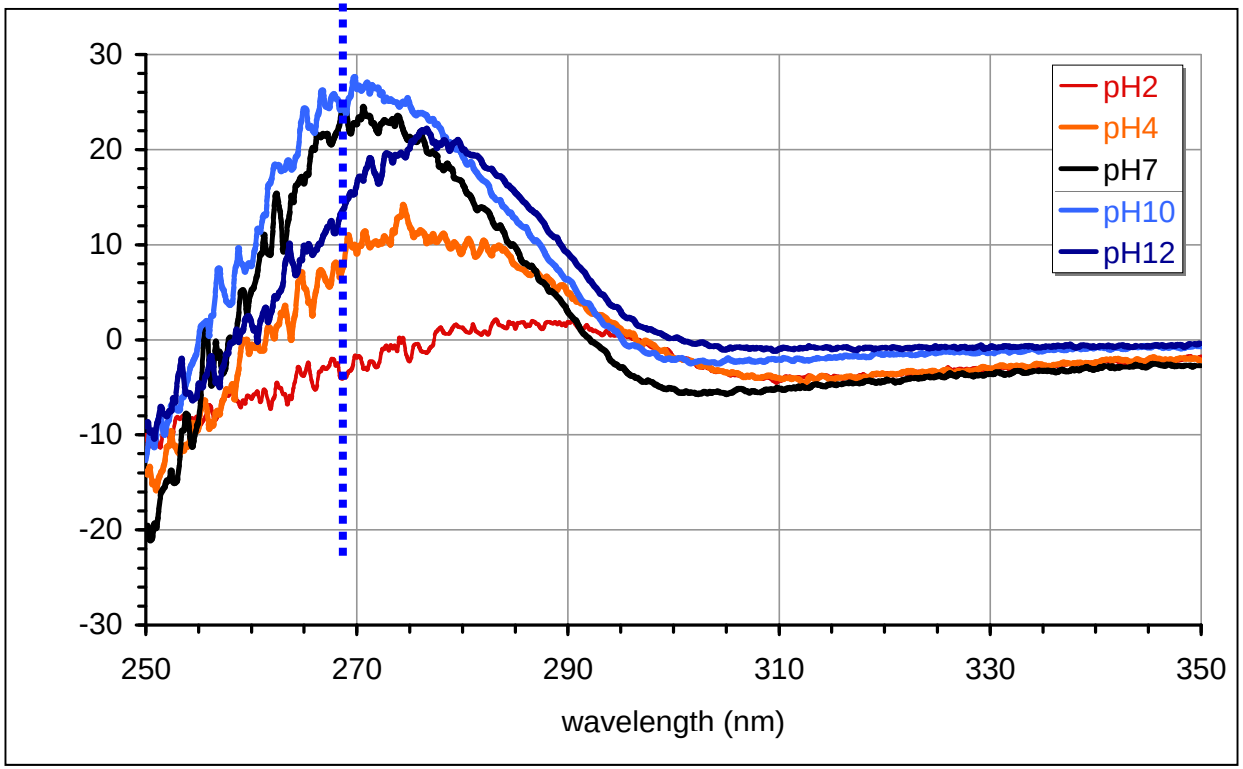
Surface adsorption properties: OWLS

pH and ionic strength dependence

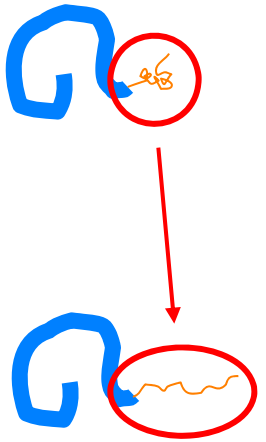


Tertiary structure: Near-UV CD spectroscopy

pH dependence



pH 7



pH 2

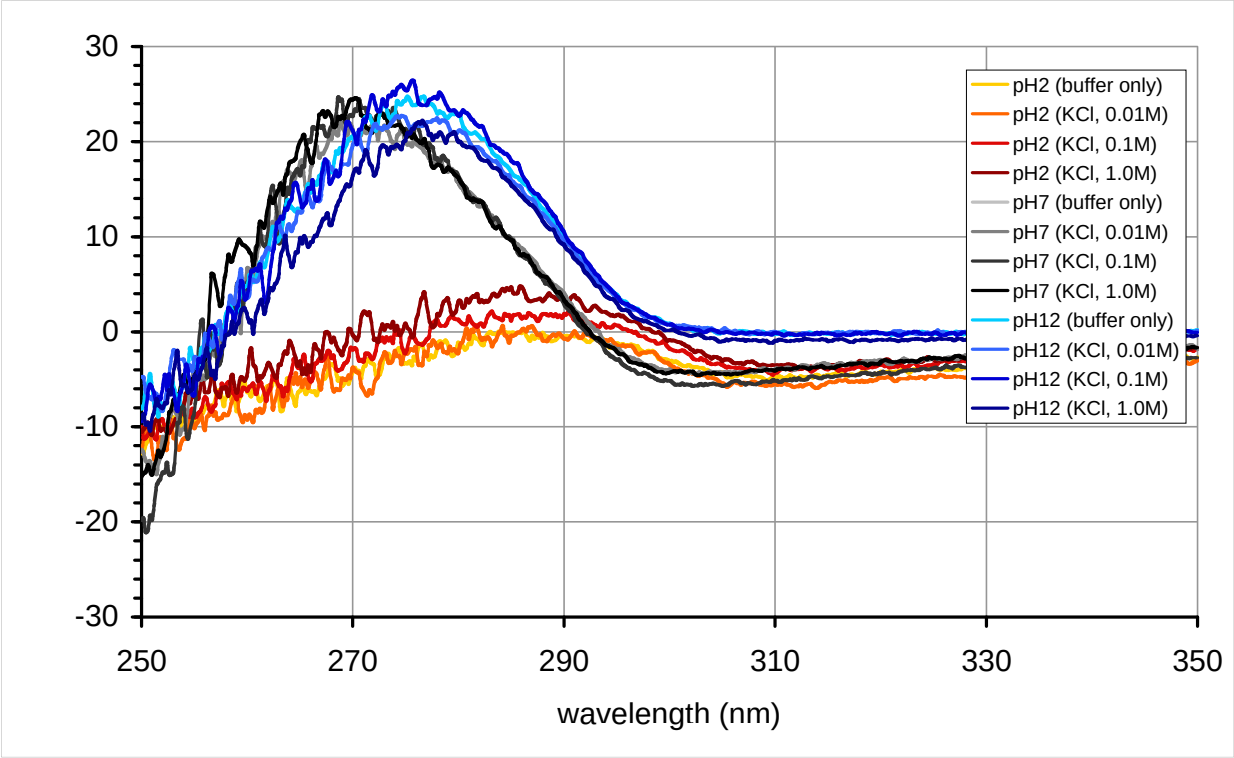
disruption of tertiary structure of “naked” polypeptide region

PGM, 1mg/ml

buffer: 1mM KH_2PO_4, KCl 0.1M

Tertiary structure: Near-UV CD spectroscopy

Ionic strength dependence



PGM, 1mg/ml

buffer: 1mM KH_2PO_4, KCl 0.1M

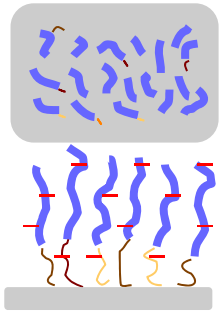
A schematic model at the sliding interface

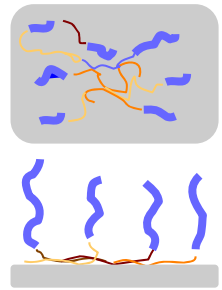
Before sliding

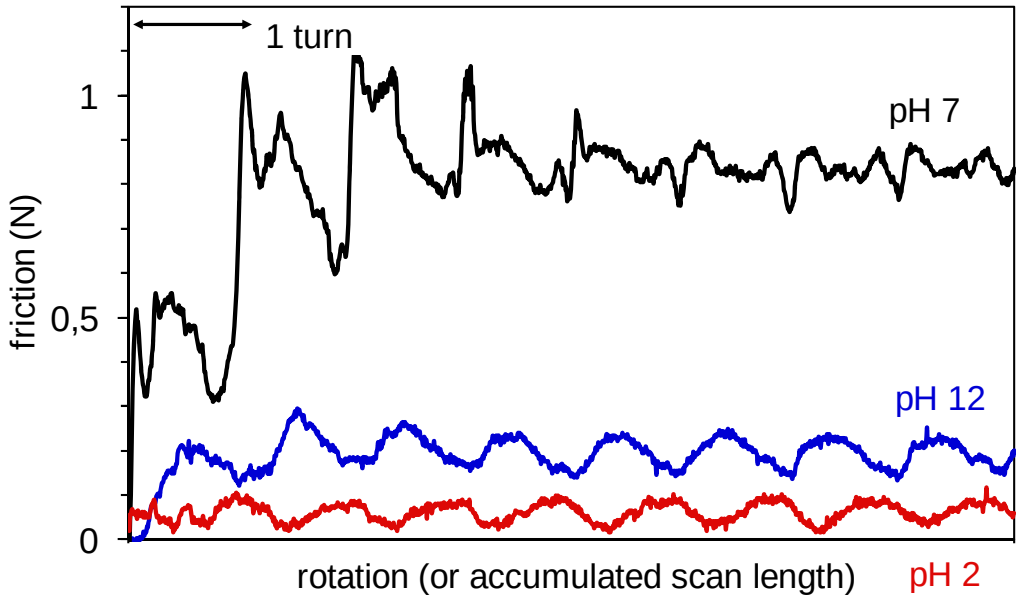
After sliding

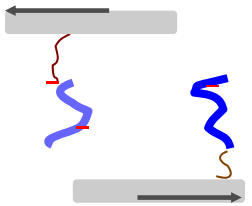
pH 7

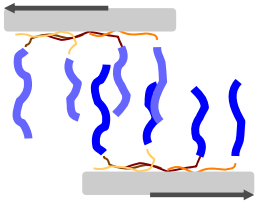
pH 2



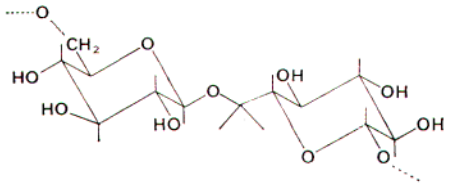




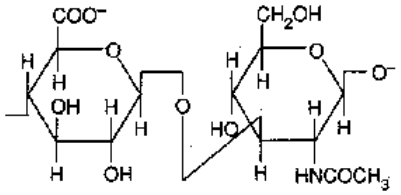




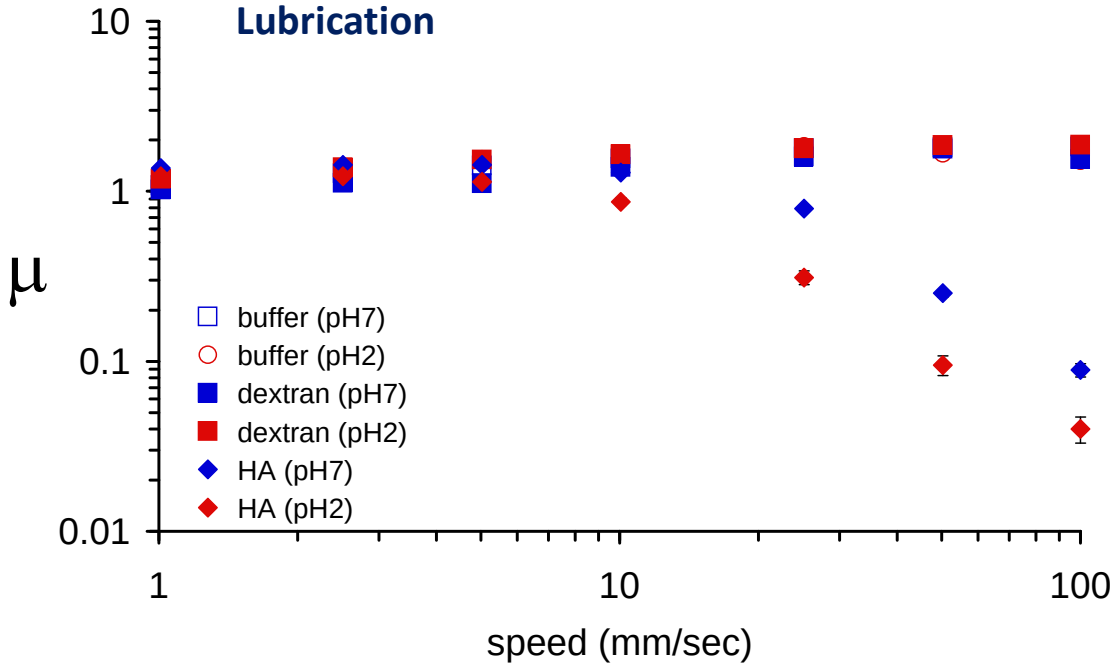
Model polysaccharides : Dextran and Hyaluronic acid

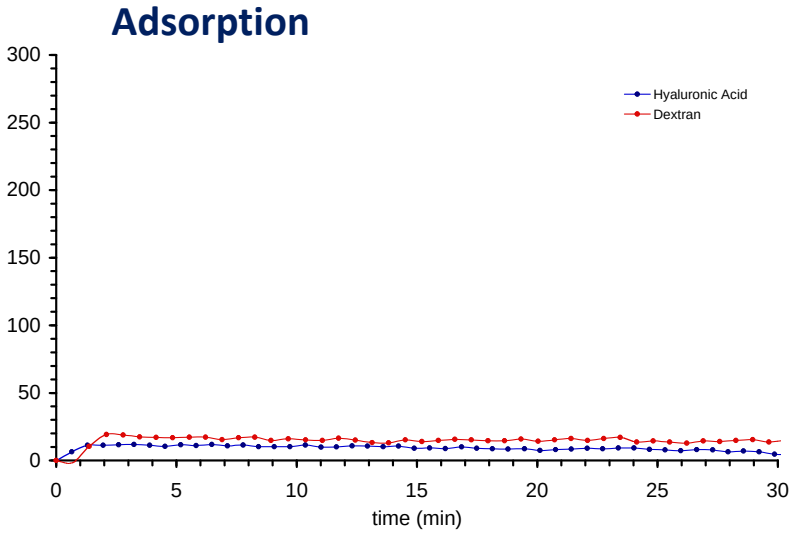


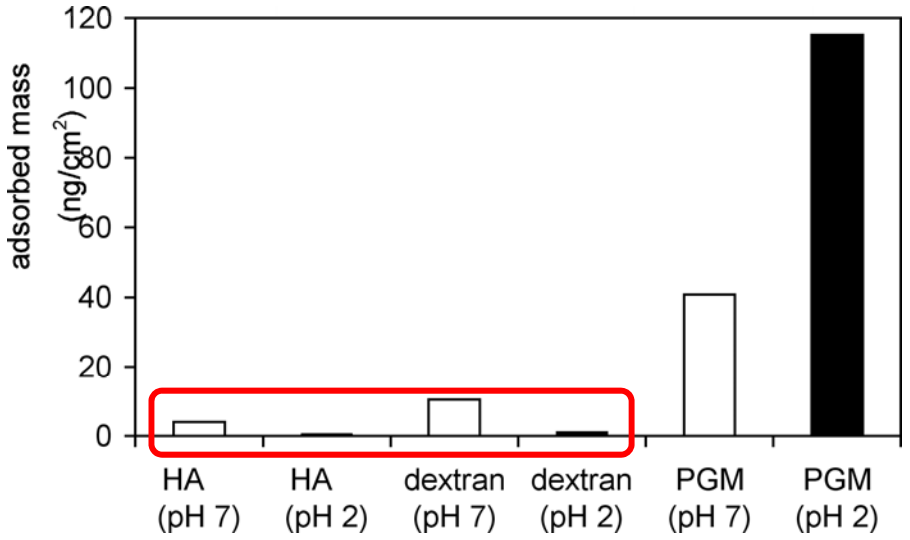
Dextran



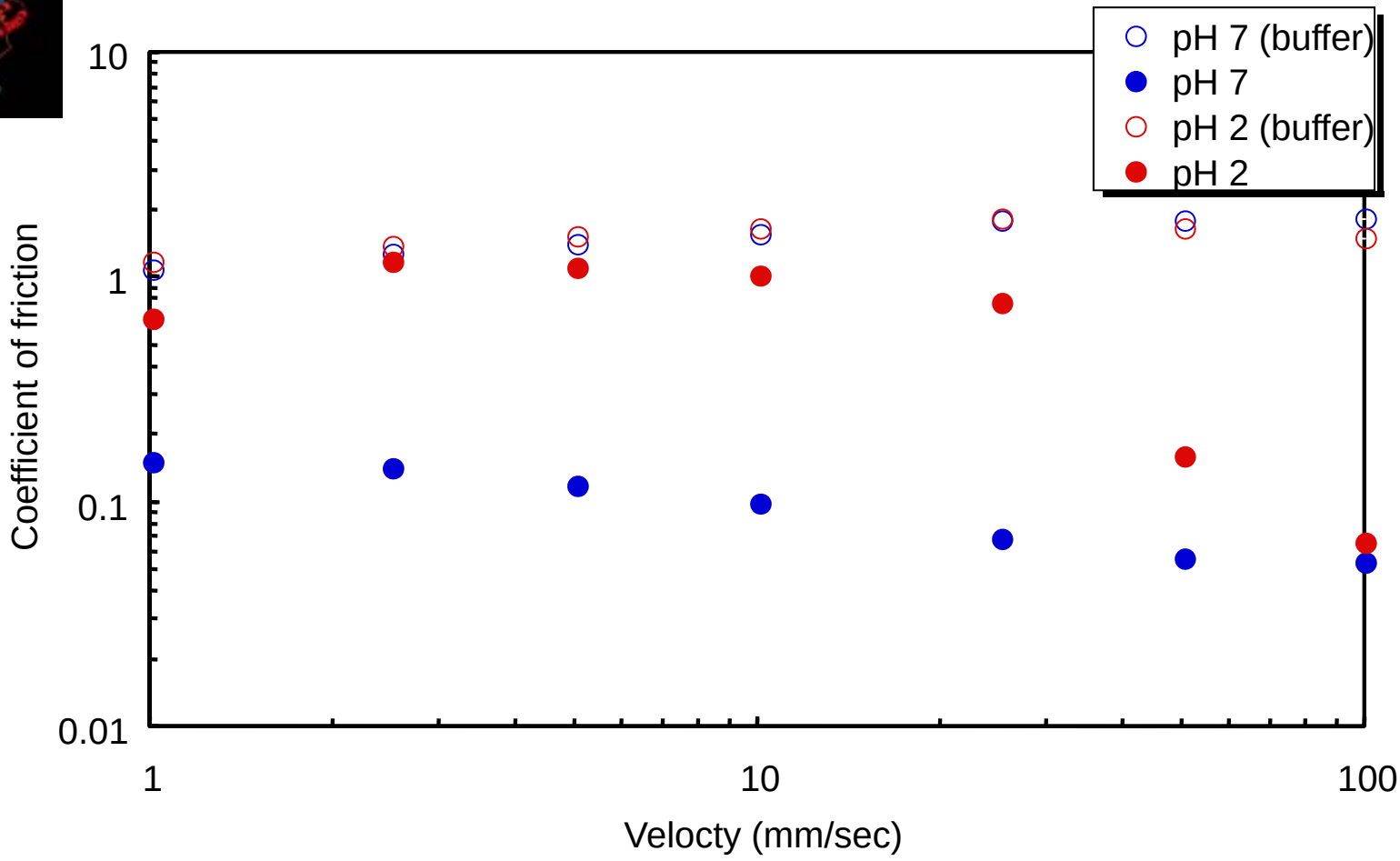
Hyaluronic acid







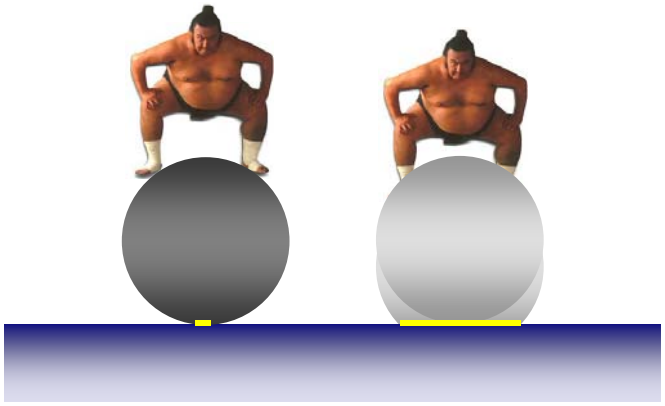
Model proteins : albumin



Load : 1 N

buffer = KH_2PO_4 10 mM

Soft Elastohydrodynamic Lubrication (soft EHL)



rigid elastic

Hamrock, Dowson, Esfahanian

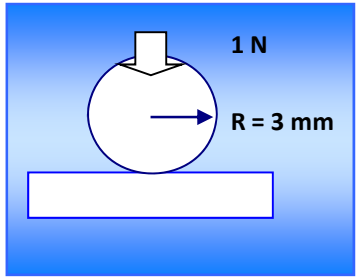
Hamrock, B.J. and Dowson, D., Proc. 5th Leeds-Lyon symp. on Trib. 22-27 (1979)

Esfahanian, M. and Hamrock, B.J., Tribol. Trans. 34, 628-632 (1991)

Hard EHL $h_{min} = 1.79\, R^{0.47} \alpha^{0.49} \eta_0^{0.68} U^{0.68} E^{-0.12} W^{-0.07}$

Soft EHL $h_{min} = 2.8\, R^{0.} \eta_0^{0.65} U^{0.65} E^{-0..44} W^{-0.21}$

α : pressure coefficient of viscosity



Soft contact: PDMS vs. PDM

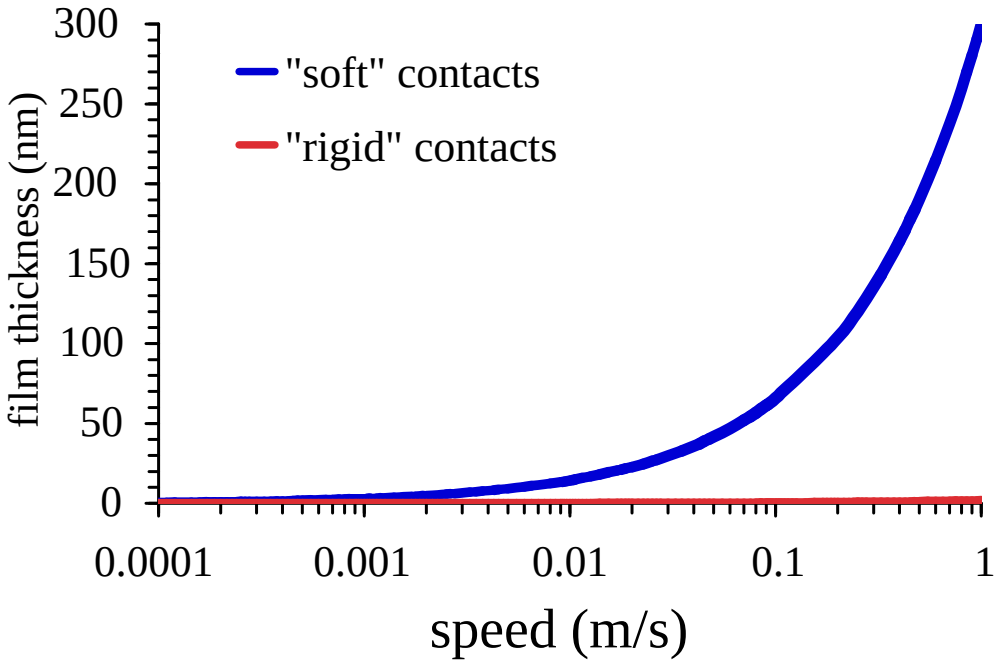
Rigid contact: steel vs. steel

E (PDMS) = 2 MPa

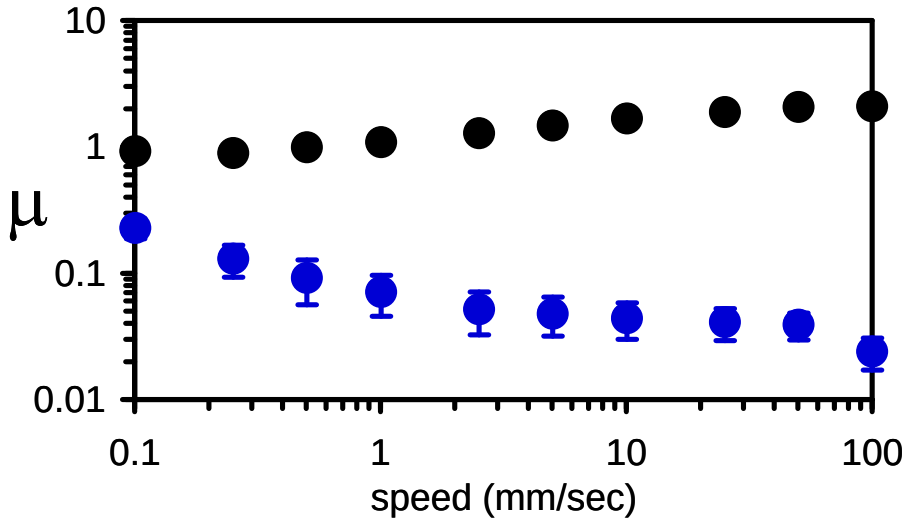
ν (PDMS) = 0.5

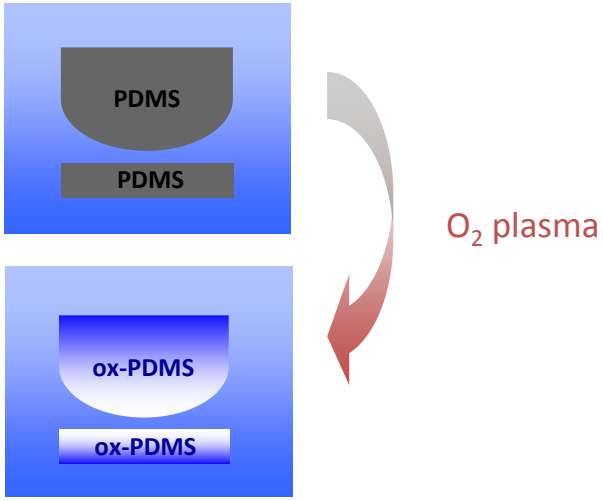
E (steel) = 200 GPa

ν (steel) = 0.3



Effect of surface hydrophilicity

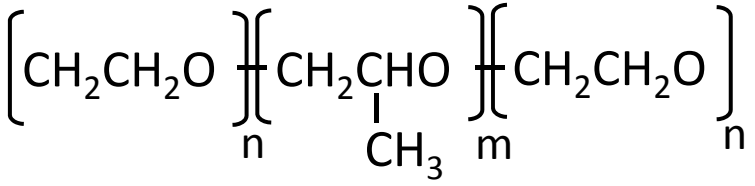




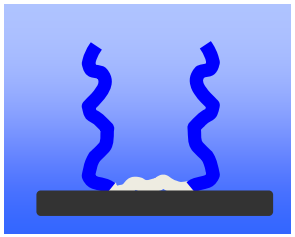
No significant change in bulk mechanical properties

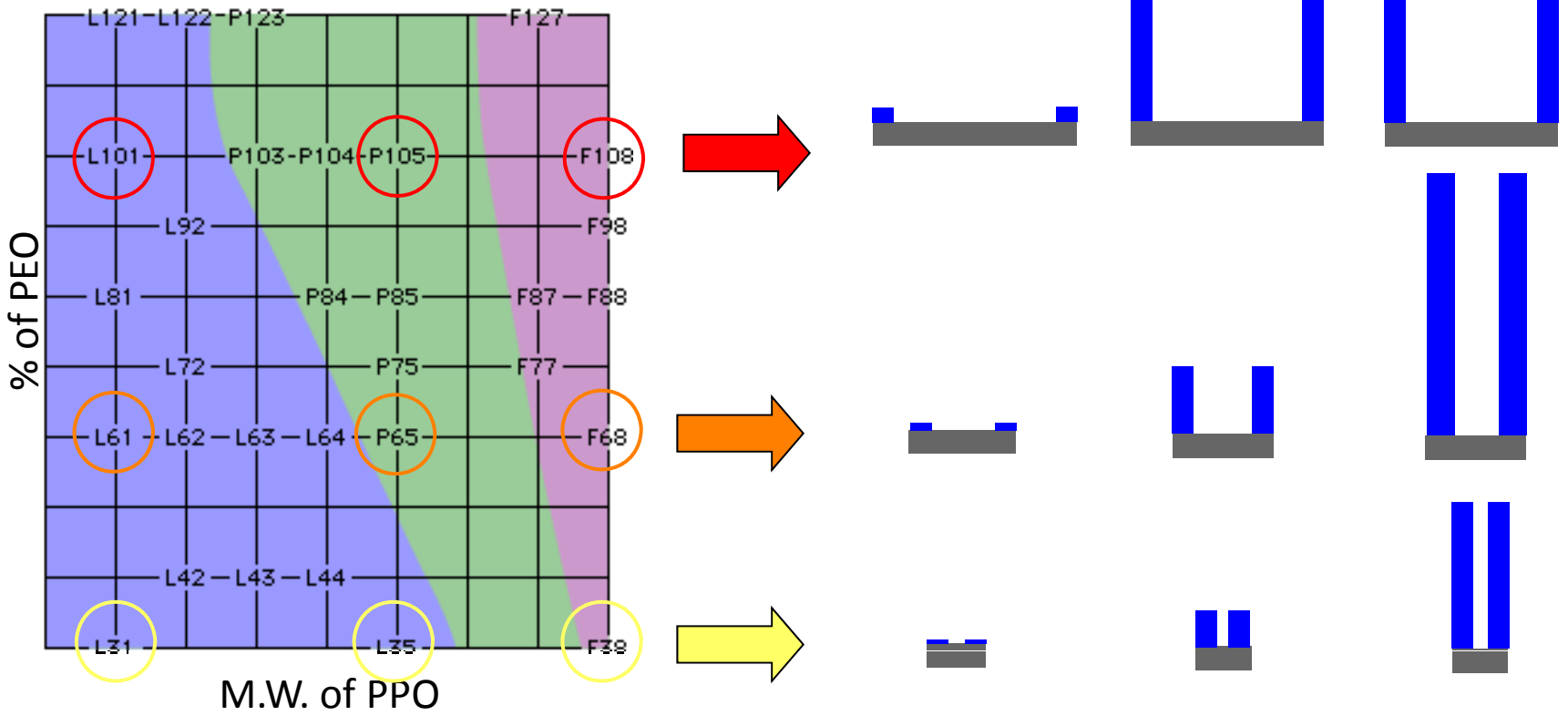
Hydrophilization of surface (-OH and/or -COOH groups)

PEO-b-PPO-b-PEO (Pluronic®)

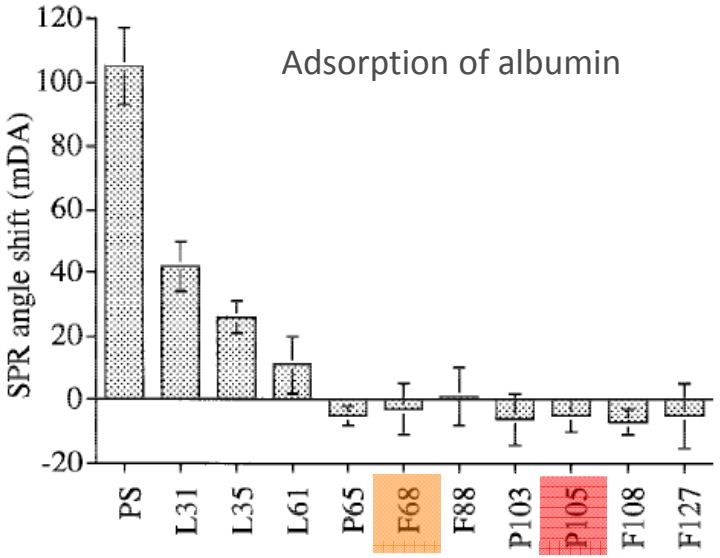


PEO-*b*-PPO-*b*-PEO

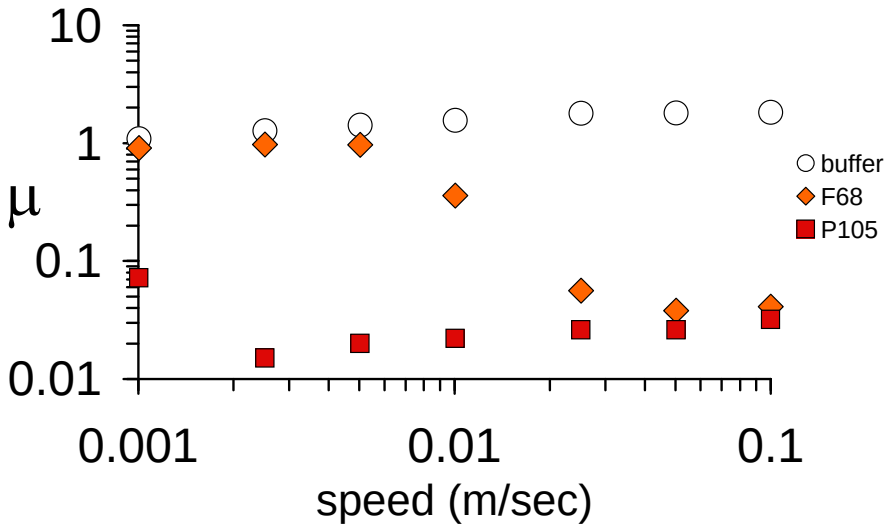


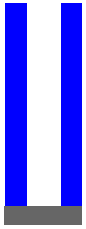


PEO-b-PPO-b-PEO



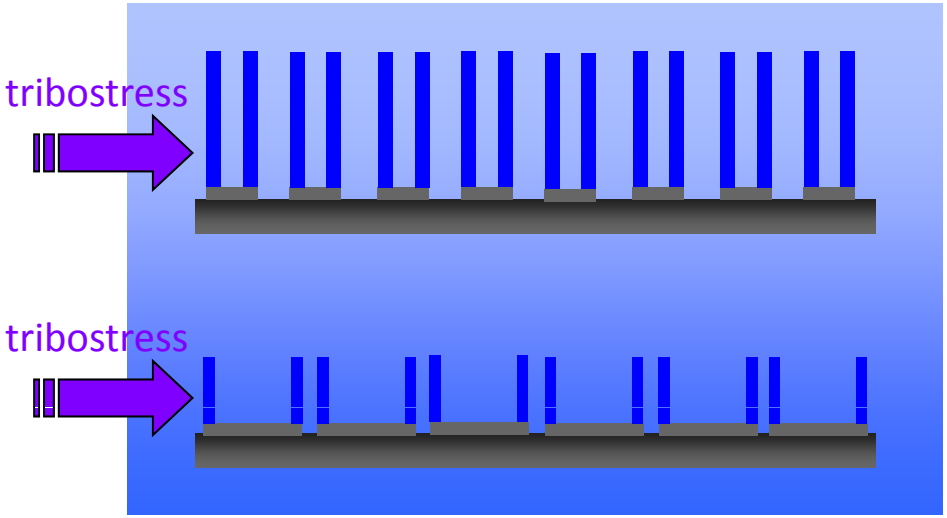
J. Biomed. Mat. Res., 1998, R.J. Green et al



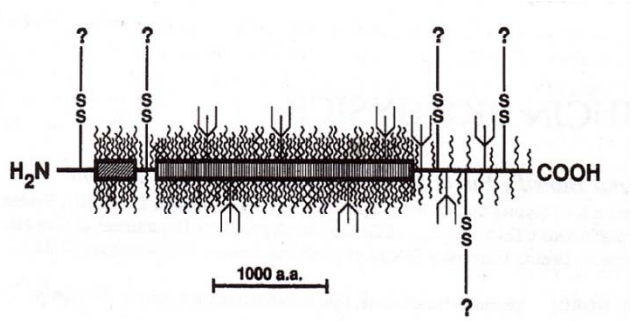


F68 $EO_{76.4}\ PO_{29}\ EO_{76.4}$

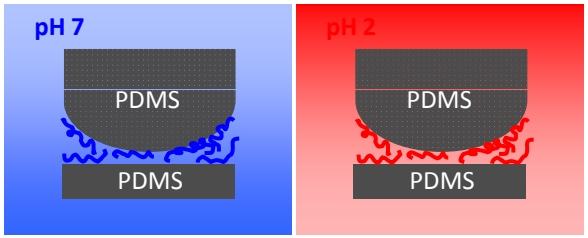
P105 $EO_{36.9}\ PO_{56}\ EO_{36.9}$

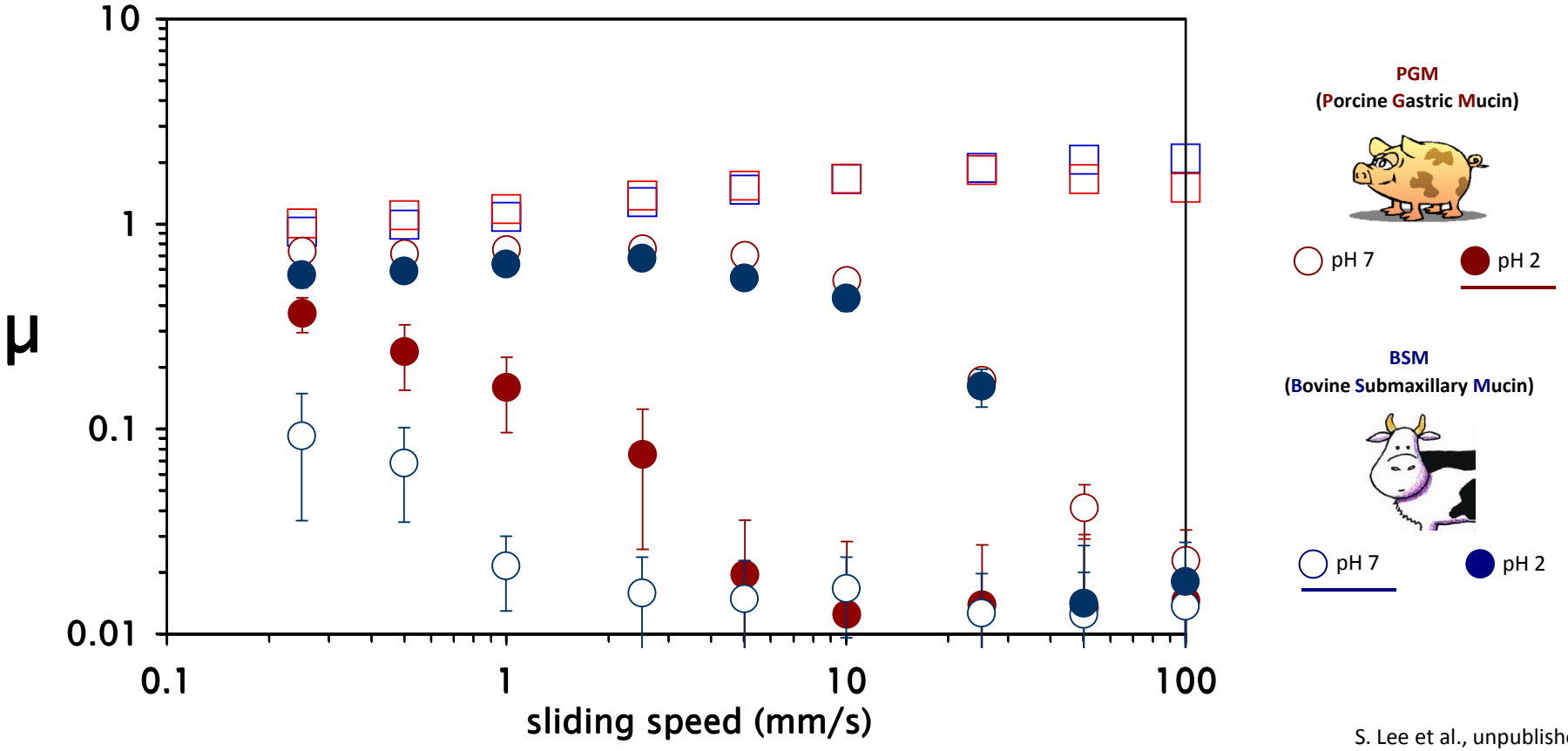


Mucins from different organs: similarity and difference



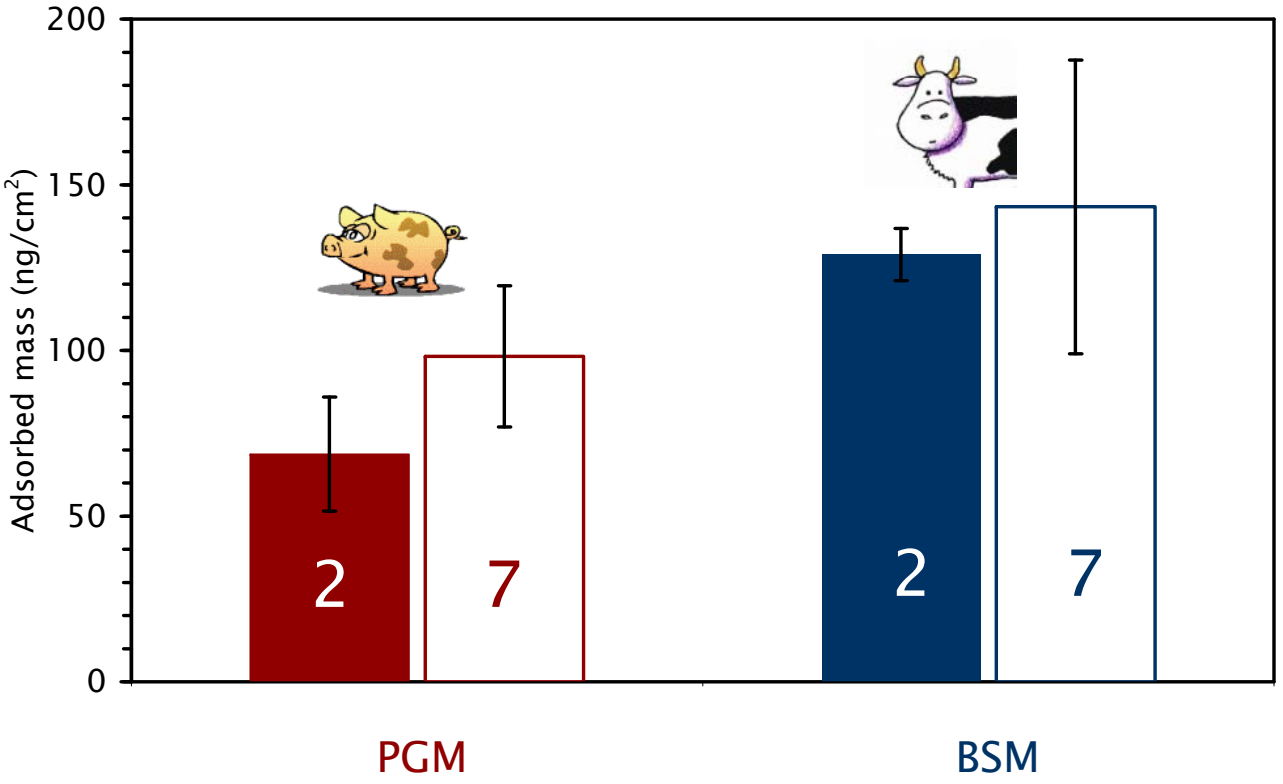
Bansil et al, **Annu. Rev. Physiol**. 1995, *57*, 635.



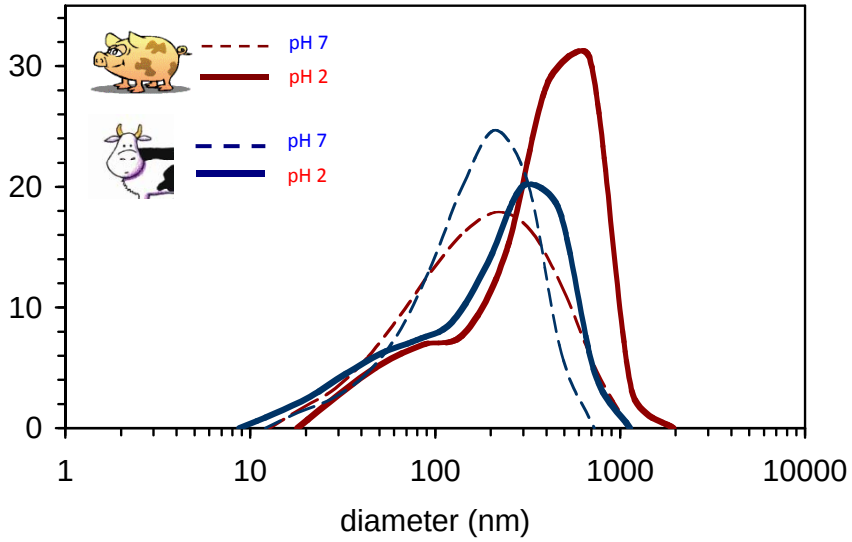


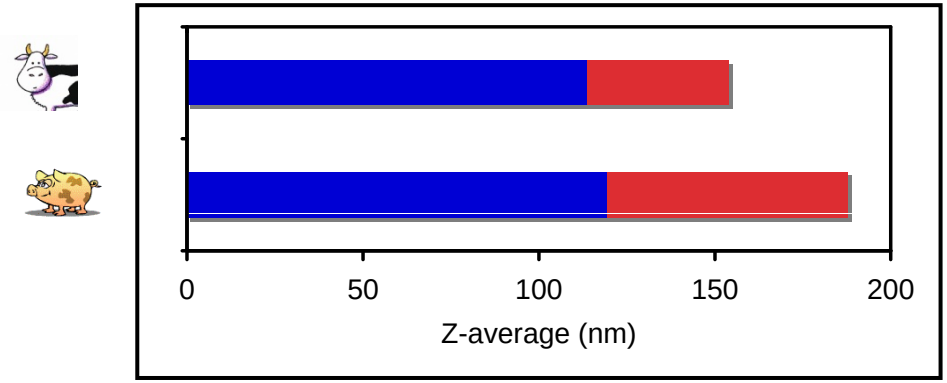
S. Lee et al., unpublished

BSM vs. PGM: Adsorption behavior



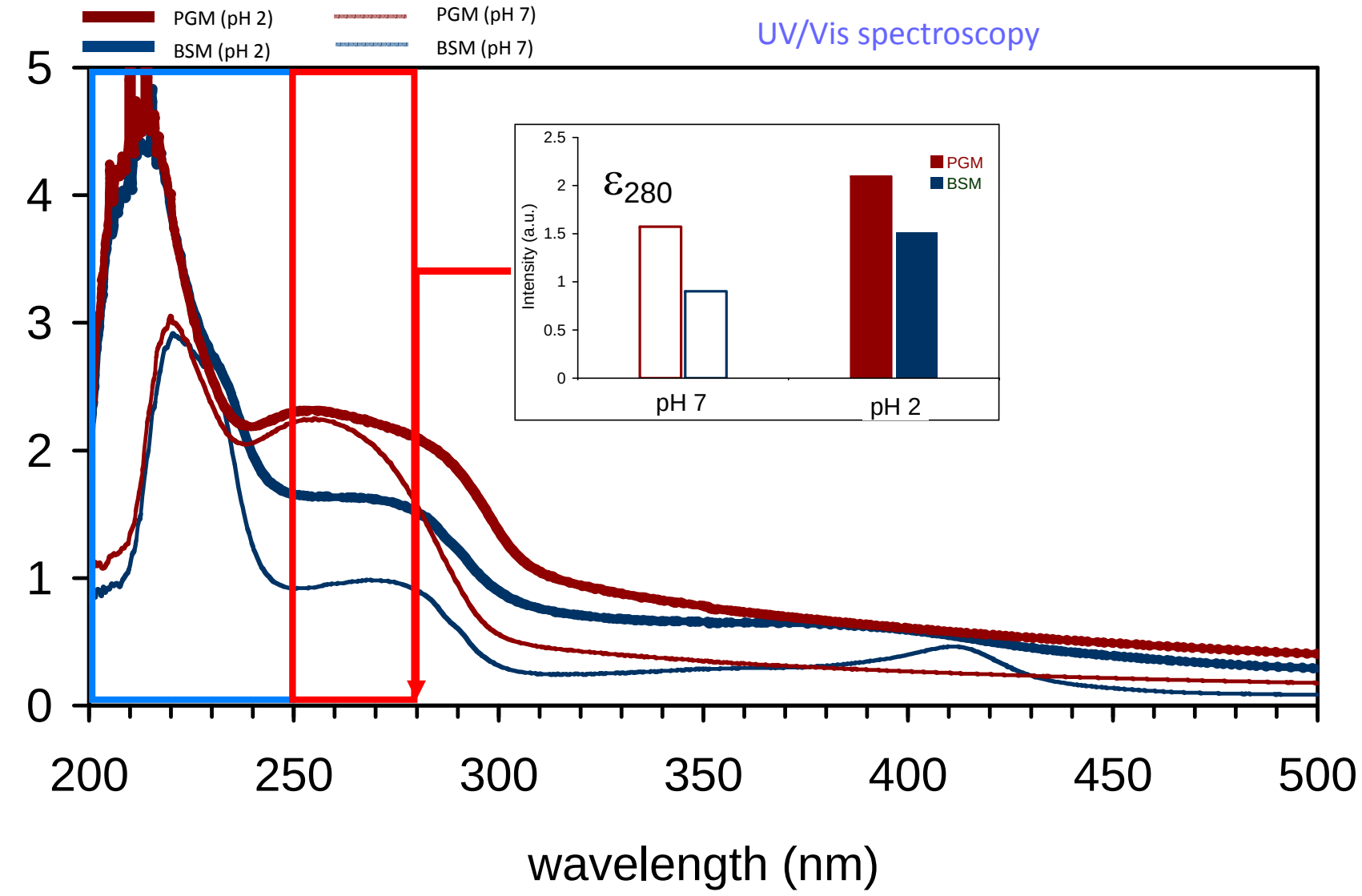
BSM vs. PGM: Size (Dynamic Light Scattering)

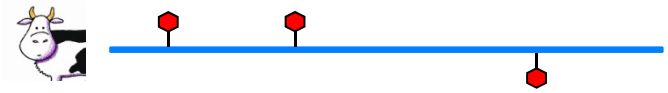




*Increase in size (**aggregation**) at pH 2 is general for both mucins, but is more pronounced for PGM than BSM*

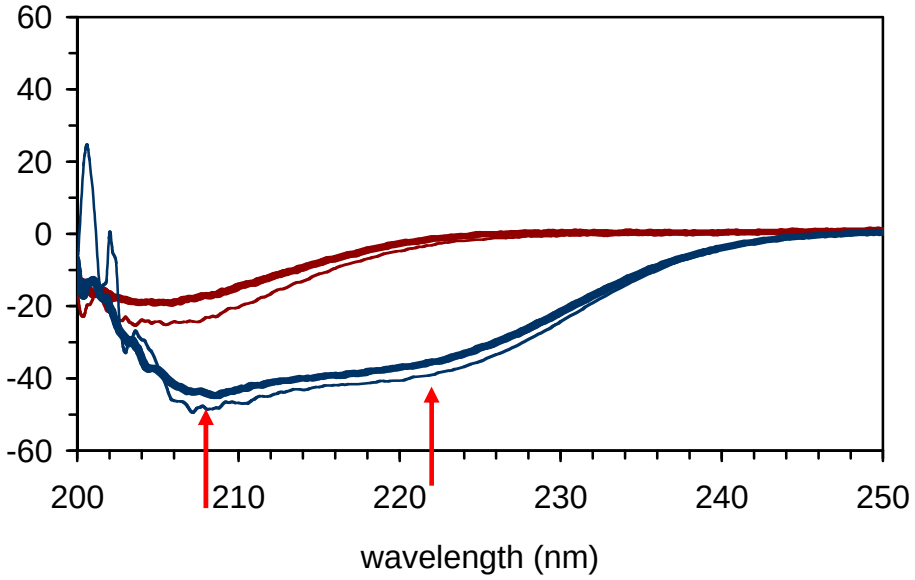
BSM vs. PGM: Protein composition



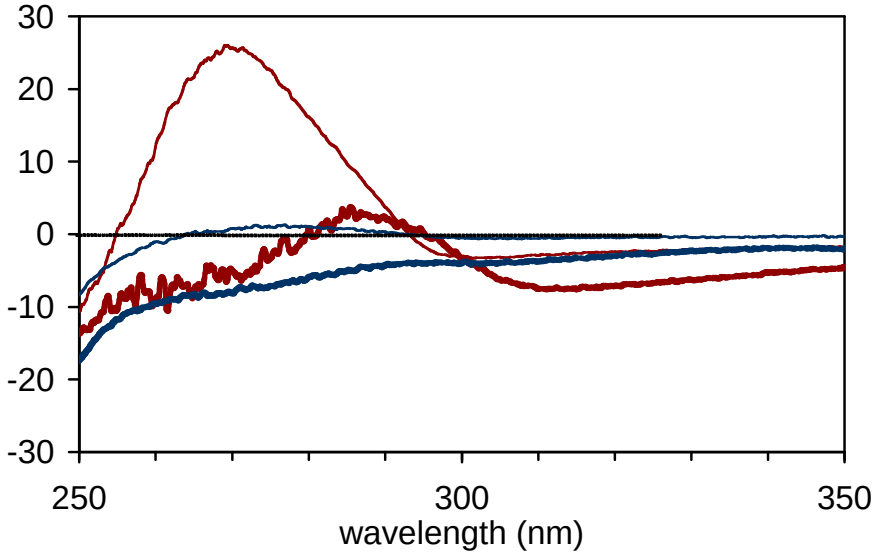


BSM vs. PGM: Protein conformation

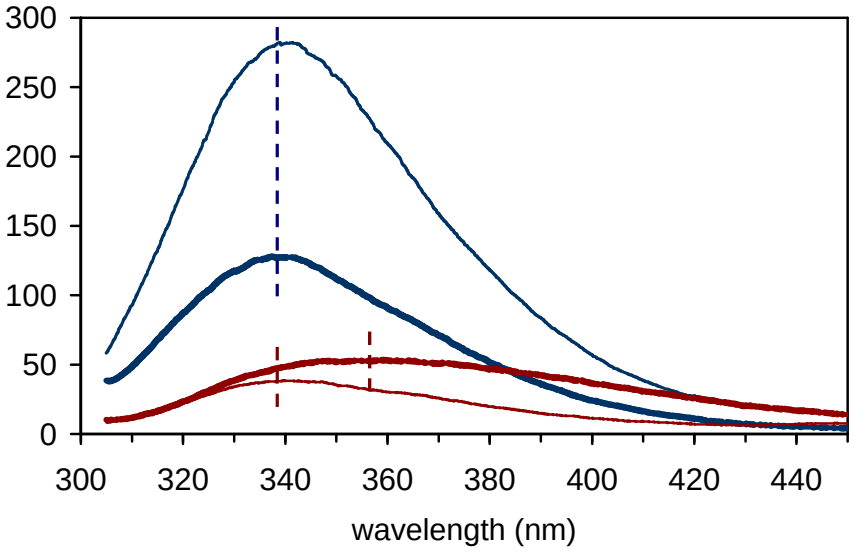
Secondary structure: Far-UV CD

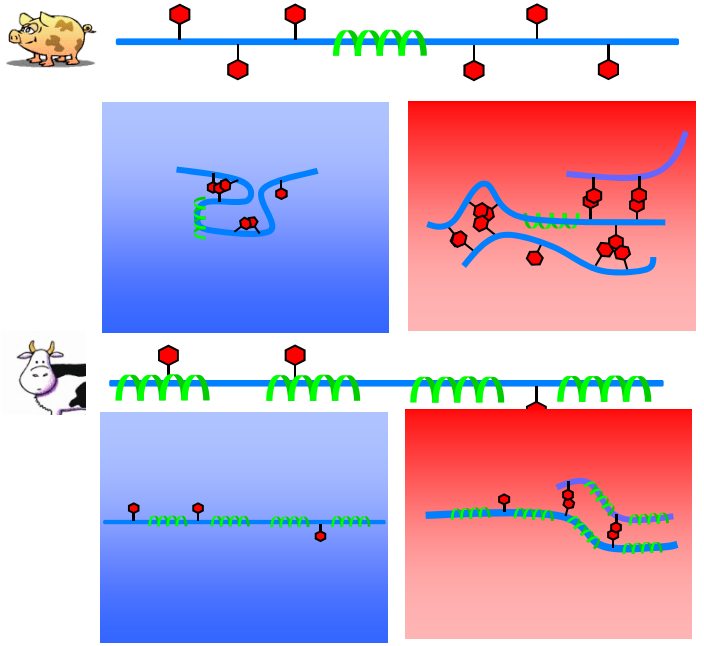


Tertiary structure: Near-UV CD

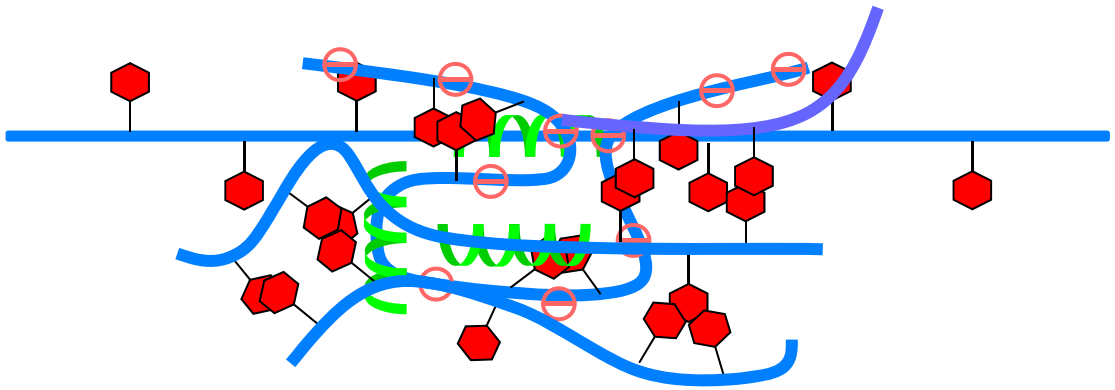


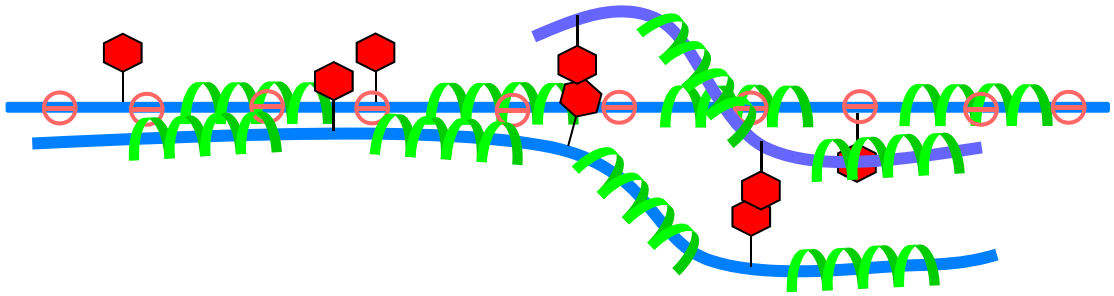
Protein unfolding: Fluorescence Spec.

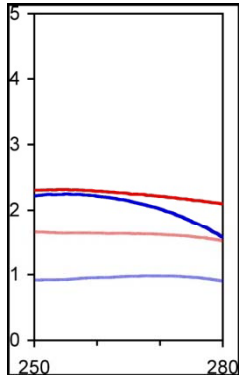


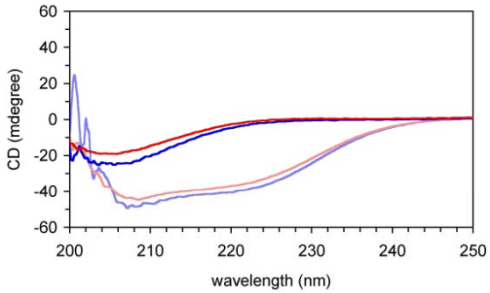


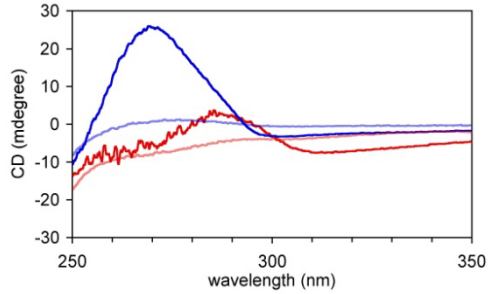
A proposed model: In bulk solution

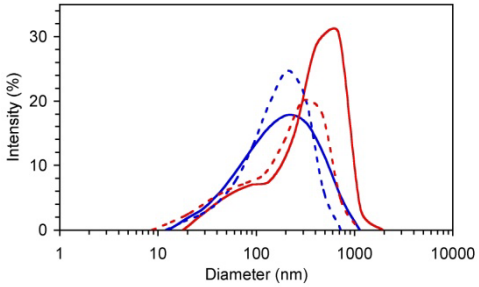




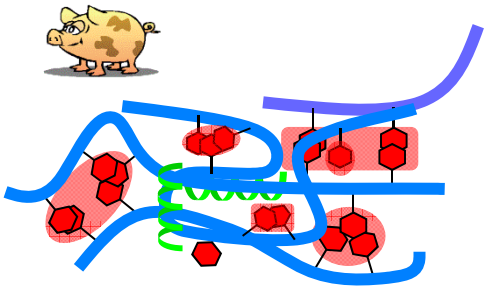


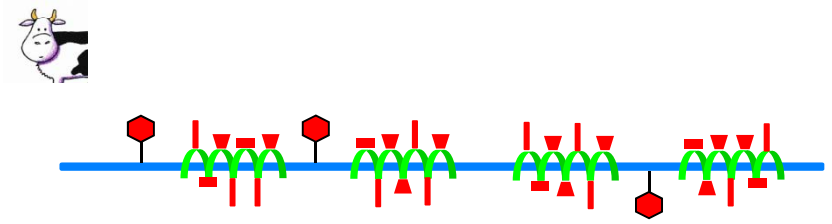






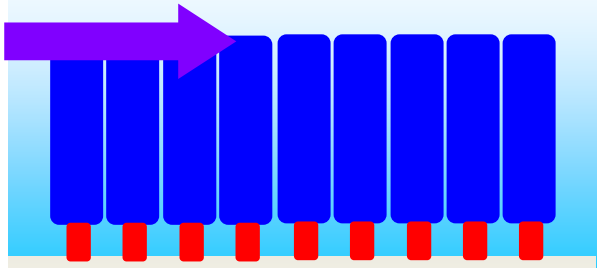
A proposed model: At liquid/solid interface

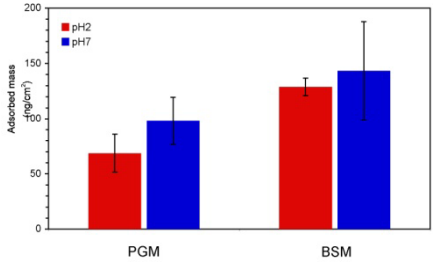




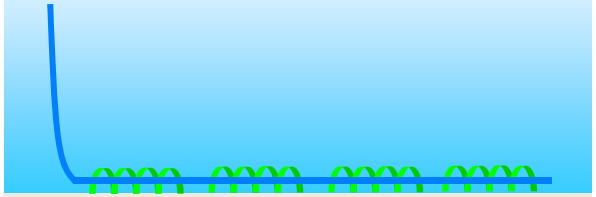
pH 7

tribostress



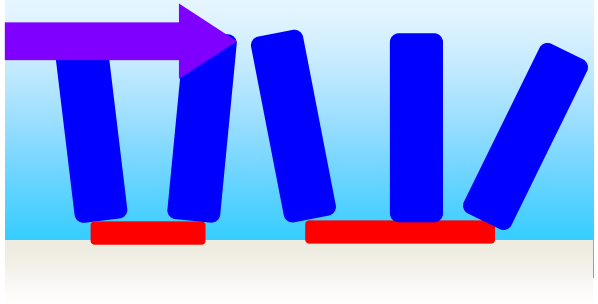


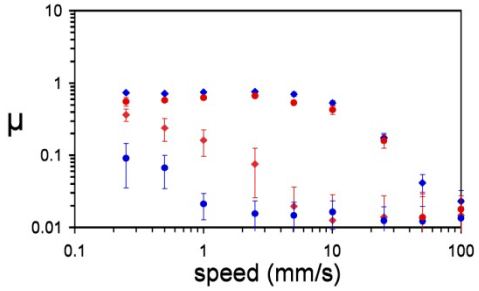
pH 7



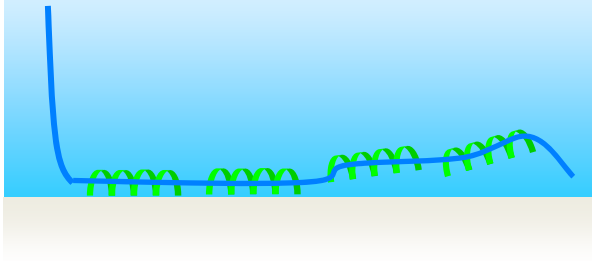
pH 2

tribostress





pH 2



Thank you for your attention!